

Measuring Low Concentrations of ^{234}Th in Water and Sediment

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Abstract

$^{234}\text{Th}/^{238}\text{U}$ disequilibria have been used extensively in studies of particle dynamics and the fate and transport of particle-reactive matter in marine environments. Similar work in low salinity, estuarine, and freshwater systems has not occurred primarily because the lower concentrations of both parent and daughter nuclides that are typical of these systems often render established methods for the analysis of ^{234}Th inadequate. The application of this radionuclide tracer technique to these systems, however, has great potential. To this end, we present a method for measuring low activities of ^{234}Th in relatively small samples (< 200 L) using low background gas-flow proportional counters, a ^{229}Th yield monitor, and empirical corrections for the interferences from real and apparent betas that are emitted by other thorium

isotopes and their progeny. For samples with low $^{234}\text{Th} / ^{228}\text{Th}$ activity ratios, we improve upon current beta-counting methodologies that rely on immediate sample counting, weak beta absorption, or multiple beta counts so that, using the analytical approach outlined here, it should be possible to measure ^{234}Th activities i) as low as 1.5 dpm / total sample, ii) up to two weeks after radiochemical purification of thorium, and iii) with only one sample count for alpha and beta activity.

1. Introduction

In marine environments, particle-reactive scavenging rates (e.g., Coale and Bruland, 1985; Gustafsson et al., 1997; Bacon and Anderson, 1982), sediment trap efficiencies (e.g., Buesseler et al., 1994), surface sediment mixing (e.g., Aller and Cochran, 1976; Carpenter et al., 1984), and vertical and horizontal particle transport rates (e.g., Kershaw and Young, 1988; McKee et al., 1984; Feng et al., 1999) have all been calculated in part by measuring disequilibria between naturally occurring, particle-reactive ^{234}Th and its generally soluble parent, ^{238}U . In many brackish and freshwater systems, however, ^{238}U and ^{234}Th activities are an order of magnitude or more lower than those found in marine systems.

Established methods used to measure ^{234}Th differ not so much with respect to thorium concentration and isolation (see e.g. Rutgers van der Loeff and Moore, 1999) but rather by mode of detection. ^{234}Th ($t_{1/2} = 24.1$ days) emits gamma (γ) radiation immediately following its decay to ^{234m}Pa by beta (β) emission. ^{234m}Pa ($t_{1/2} = 1.2$ min.) subsequently decays by beta emission to ^{234}U . These emissions can be measured using gamma spectrometers and gas-flow proportional (beta) counters.

Each method of detection (γ and β) has its advantages and drawbacks. On one hand, sample preparation for gamma spectrometry is relatively simple and nondestructive. Gamma spectrometry can also identify and quantify individual radionuclides. However, low photon abundance combined with relatively low detector efficiencies typically result in only ~ 1.5 γ cpm per 100 dpm of ^{234}Th (Buesseler et al., 1992). Consequently, the measurement of ^{234}Th by gamma spectrometry has required a sample size of at least 500 to 5000 liters of seawater. To extend this method to fresh water, where ^{234}Th activities can be over an order of magnitude lower, would require a proportionate increase in sample

size. Handling samples of this size on the small research vessels or at remote land-based sites commonly encountered in sampling estuarine and freshwater systems would be, at best, cumbersome, if not very difficult.

Low background gas-flow proportional counters, on the other hand, are very efficient at detecting beta radiation with combined counting efficiencies near 100% for the $^{234}\text{Th} + ^{234m}\text{Pa}$ pair. High detector efficiencies and low instrument backgrounds permit very low detection limits for these beta-emitting nuclides so that current ^{234}Th beta counting methods require a sample size of only 2 to 20 liters of seawater (Buesseler et al., 2001; Benitez-Nelson et al., 2001). Unlike gamma spectrometry, however, individual beta sources cannot be distinguished through proportional counting alone.

The major problem associated with beta counting ^{234}Th in natural samples is the unknown contribution of beta counts from (i) the ingrowth of beta producing progeny from ^{228}Th (and ^{229}Th , if added as an isotopic diluent); and (ii) internal conversion electrons from the alpha decay of ^{228}Th , ^{229}Th , ^{230}Th and ^{232}Th . The contribution of extraneous (i.e. non- $^{234}\text{Th} + ^{234m}\text{Pa}$) and apparent (i.e. internal conversion electron) beta counts to the gross beta count will vary, of course, depending on the sample source and matrix. In the open ocean, where ^{234}Th is nearly in secular equilibrium with its parent, the activity ratio of ^{234}Th to other naturally occurring thorium isotopes is on the order of 10^3 to 10^4 (Broecker and Peng, 1982). Under these conditions, interference from the naturally occurring, alpha-emitting thorium isotopes to the $^{234}\text{Th} + ^{234m}\text{Pa}$ beta count can be assumed to be negligible. However, at very low ^{234}Th activities found in certain estuarine and freshwater environments, the activity ratio of ^{234}Th to other naturally occurring thorium isotopes decreases substantially and extraneous and apparent beta counts originating from these other thorium isotopes must be taken into account.

Corrections for these non- $^{234}\text{Th} + ^{234m}\text{Pa}$ beta counts are typically made in one of three ways which we will define as 1) the immediate sample count method, 2) the weak beta absorber method, and 3) the multiple beta count method.

The “immediate sample count” method relies simply on counting the sample immediately after thorium separation and preparation of the beta source (planchet). While this minimizes the in-growth of

extraneous (non- $^{234}\text{Th} + ^{234m}\text{Pa}$) beta counts originating from ^{228}Th (and ^{229}Th) progeny, it does not take into account the contribution of apparent beta counts from internal conversion electrons.

The “weak beta absorber” method relies on counting only the high-energy betas of ^{234}Th ’s daughter, ^{234m}Pa (Emax: 2.29 MeV), by selective removal of weak energy betas through the use of an absorber (e.g. a piece of aluminum foil) between the sample and gas-flow proportional counter. This absorber method, however, is not appropriate for samples containing any significant activity of ^{228}Th or ^{229}Th because both isotopes rapidly produce progeny that also give off high-energy betas (e.g. ^{212}Bi : Emax: 2.25 MeV and ^{213}Bi : Emax: 1.42 MeV) that cannot be selectively absorbed or distinguished in the presence of ^{234m}Pa (Baltakmens, 1977). Decreasing the $^{234}\text{Th} + ^{234m}\text{Pa}$ beta signal will also necessitate an increase in sample size at very low ^{234}Th concentrations.

The “multiple beta count” method requires counting the sample beta source repeatedly (e.g. 2 to 6 times) over a period of up to 6 half lives of ^{234}Th (~ 145 days). By fitting an exponential curve with a decay rate of 24.1 days to the gross beta count (Buesseler et al., 2001), or alternatively, by plotting the gross beta count rate of the thorium sample as a function of $e^{-\lambda t}$, where λ is the decay constant of ^{234}Th and t is the time elapsed since separation of ^{234}Th from its parent ^{238}U in the sample (Aller and Cochran, 1976), the initial activity of ^{234}Th in the sample can be calculated from the slope of the decay line. However, for samples containing relatively high activities of ^{228}Th , there are constraints on the timing of the initial beta count. Because the in-growth of beta producing nuclides from ^{228}Th (and to a lesser extent ^{229}Th) has a similar time scale as the rate of ^{234}Th decay, the true slope of ^{234}Th decay will be masked until the other beta producing nuclides reach transient (or secular) equilibrium. For ^{228}Th , this takes ~ 3 weeks. Determining the activity of a single sample using the multiple-count method, therefore, may take months. Furthermore, the initial activity of ^{234}Th in the sample must be high enough so that it can be counted at least three weeks after sample collection. If not, the sample size must increase.

In view of these limitations, we present here a new approach to measuring low concentrations of ^{234}Th in samples with low $^{234}\text{Th} / ^{228}\text{Th}$ activity ratios by directly assessing beta interferences from each of the alpha emitting thorium isotopes in the sample.

2. Experimental Section

A flowchart showing our approach to measure both dissolved and particle-bound ^{234}Th fractions in a water (or sediment) sample is presented in figure 1.

2.1. Sample Collection and Preparation.

An initial estimate of the amount of water and sediment needed to measure ^{234}Th may be determined by first measuring the dissolved ^{238}U activity in the sample matrix (Kaplan et al., 1994; Edgington et al., 1996). In Lake Michigan, where samples for this study were collected, ^{238}U activities in the water averaged 0.23 ± 0.02 dpm L^{-1} ($n = 12$). Accordingly, we ascertained that 100 to 200 liters of Lake Michigan water would be more than sufficient to measure both dissolved and particle-bound ^{234}Th fractions.

Water samples (200 L) were collected using a submersible pump and stored briefly in 50 L plastic containers until separation of the phases by filtration. The particle-bound thorium fraction on suspended sediment was separated from the water sample by filtration through pre-weighed nitrocellulose filters (0.45 μm , 293 mm, Millipore) – usually within 2 hours of collection. The time of filtration (t_{la}) was noted and the filter was stored at 4°C until it could be dried at 60°C and weighed to determine the mass of total suspended solids.

One hundred liters of the filtrate were placed in a 200-liter plastic conical container for the recovery of the dissolved thorium fraction (operationally defined by the filter pore size). The thorium was co-precipitated onto newly formed iron hydroxide and the precipitate immediately separated by filtration. In detail, the initial filtrate was acidified with 500 ml of concentrated HCl (12M), and the requisite

aliquot portion of the isotopic diluent, ^{229}Th (e.g. 0.4 dpm), was added and stirred vigorously for 15 minutes. Next, 1 mg L^{-1} ferrous iron was added as ferrous sulfate (i.e. 0.5 grams) and the solution was again well stirred for a few minutes. Ferric hydroxide was precipitated by adding 500 ml of concentrated NH_4OH (14M) and this precipitate was immediately collected onto a nitrocellulose filter (0.45 μm , 293 mm, Millipore). The time of filtration (t_{fb}) was recorded and the filter was stored at 4°C . The formation of ferric hydroxide by the oxidation of Fe^{2+} produces a more easily filterable precipitate than one produced directly from the addition of Fe^{3+} , which tends to clog the filters.

2.2. Chemical Separation of Thorium

Filters carrying the small amounts of either the particulate or precipitated thorium fractions were moistened with deionized water and combusted in a muffle furnace at 520°C for eight hours.

2.2.1. Dissolved Fraction – The ashed ferric hydroxide precipitate was dissolved in 20 ml of 6M HCl in a 250 ml glass beaker and gently evaporated to a moist residue. The residue was then taken up in 20 ml of 8M HNO_3 .

2.2.2. Particle-bound Fraction – The ashed sediment fraction was reweighed to determine sample loss on ignition and transferred to a 600 ml glass beaker. The requisite isotopic diluents (e.g. 0.4 dpm of ^{229}Th and 0.2 dpm of ^{236}U) and 50 ml of 6M HCl were then added to the sediment sample. The beaker was covered with a watch glass and heated to just below boiling point for 8 hours. The leachate was then centrifuged to remove any insoluble residue. Another 50 ml aliquot of 6M HCl was added to the once-leached sediment and the leaching process was repeated. The combined $\sim 100\text{ ml}$ of leachate were evaporated to a moist residue and then re-dissolved in 20 ml of 8M HNO_3 prior to column separation.

2.2.3. Separation of thorium using ion-exchange – Thorium was isolated from uranium and all other elements by separation on an anion ion-exchange column (Edgington et al., 1996; Faris and Buchanan, 1964). Disposable small columns were prepared using glass Pasteur pipettes (8.5 cm x 0.6 cm, Fisher Scientific) and filled with anion exchange resin (BioRad, AG1-X8, 100-200 mesh) to give a 7 cm

column (approx. 0.8 g of resin). The anion exchange resin column was first converted to the nitrate form using a 5 ml aliquot portion of 8M HNO₃. The entire sample was then transferred to the top of the column and allowed to elute before washing with an additional 20 ml of 8M HNO₃ in four 5 ml aliquot portions. The eluate was saved for later analysis of the small amount of ²³⁸U carried along with the thorium in the precipitation (dissolved fraction) or leaching (particle-bound fraction) stage.

Only thorium and plutonium were retained on the resin at this point. Thorium was separated from plutonium and eluted from the column by washing with 20 ml of concentrated HCl (12M) in four 5 ml aliquot portions. The time of elution (t₂) was noted, since in-growth of thorium progeny began at this point.

2.2.4. Electrodeposition – The separated thorium isotopes were finally transferred to a stainless steel counting planchet by electrodeposition to provide an essentially weightless source. In detail, the concentrated HCl solution containing the thorium fraction was evaporated to near dryness, re-dissolved in 16 ml of a 1M ammonium chloride – 0.01M oxalic acid plating solution, transferred to a plating cell and electroplated (20V, 0.85A, 60 minutes) onto a stainless steel planchet using the technique of Puphal and Olsen (1972). Typically, using all steps in this method, from the collection of water to electrodeposition, the efficiency of recovery, based on separate experiments with ²²⁹Th is better than 95%.

2.3. Sample Counting

The sample planchet was first counted using a low background (~0.7 cpm) gas-flow proportional counter with 2 ¼ inch diameter detectors and anti-coincidence circuitry (G542 System, Gamma Products, Inc.) for four 500-minute periods to obtain total (gross) beta counts. The planchet was then counted using a silicon surface barrier detector to determine the activities of ²²⁸Th, ²²⁹Th, ²³⁰Th and ²³²Th by α-spectrometry. Total alpha count times were activity dependent, but typically ranged between 7,000 to 14,000 minutes.

2.3.1. Corrections for beta nuclide in-growth and other interferences – Beta counts originating from the in-growing progeny of ^{228}Th and ^{229}Th and apparent beta contributions from internal conversion electrons provide the sources of a positive bias to the $^{234}\text{Th} + ^{234\text{m}}\text{Pa}$ beta count. To correct for this bias, standard solutions of ^{228}Th , ^{229}Th , ^{230}Th and ^{232}Th (with some ^{228}Th present) were first purified using anion exchange (as outlined in section 2.2.3.) and electrodeposited onto separate stainless steel planchets. Each planchet containing a freshly isolated thorium isotope was then immediately placed into a gas-flow proportional counter and counted, repeatedly, for 500-minute periods over an interval of 14 days (or longer). The planchets were finally counted using α -spectrometry in detectors of known efficiency to determine specific plate activities of each thorium isotope. These counts were then used to prepare correction algorithms for the beta count contribution from each α -active isotope to the gross beta count.

2.3.2. Detector efficiencies – Detector efficiencies were evaluated for both gas-flow proportional (β) and silicon surface barrier (α) detectors. To accomplish this, a secondary standard of isotopically pure ^{238}U was first isolated from its ^{234}Th progeny on an anion exchange column in 9M HCl. The pure ^{238}U was then electrodeposited onto a stainless steel planchet and counted in a NIST calibrated (SRM 4904L-F-72) 2π alpha counter (windowless type). The calibrated ^{238}U planchet was then counted in each of the α -detectors to determine specific detector efficiencies. Next, the calibrated ^{238}U planchet (with ingrowing $^{234}\text{Th} + ^{234\text{m}}\text{Pa}$) was counted repeatedly for ten or more 500-minute cycles in each beta detector. The gross beta count rate for each counting cycle was plotted against $1 - e^{-\lambda t}$ where λ equals the decay constant for ^{234}Th and t is equal to the elapsed time (in days) between the column separation of uranium and the beta count. The effective efficiency of the beta detector (cpm/dpm) was then calculated as the slope of the ingrowth line (which equals the beta count rate (cpm) of ^{234}Th in secular equilibrium with its ^{238}U parent on the planchet) divided by the known activity of ^{238}U (dpm) on the planchet.

3. Results and discussion

3.1. Sample Preparation and Chemical Separations

There are a number of methods that can be used to concentrate and isolate thorium from the sample matrix (see e.g. Rutgers van der Loeff and Moore, 1999; Buesseler et al., 2001). Many of these methods, however, are truly applicable only in the open ocean. While the approach we outline here may seem labor intensive, there are few if any shortcuts that can be taken with the analysis of samples containing low concentrations of ^{234}Th . In particular, we suggest that the co-precipitation of thorium in the dissolved phase and isotope dilution with ^{229}Th followed by radiochemical separation of thorium by ion-exchange chromatography is the simplest and most accurate approach to measuring ^{234}Th in low salinity and freshwater systems.

While it has been shown that manganese dioxide impregnated nylon filters are effective in extracting thorium from seawater (Buesseler et al., 1992), this technique is not totally applicable for measurements of ^{234}Th in freshwater systems. Freshwater systems are more diverse and geochemically heterogeneous than oceanic waters and the calibration of MnO_2 filters would be complicated by (1) the variable composition in terms of DOM and alkalinity which strongly affect the formation of both Th and U complexes and thus adsorption to the filter; (2) the effect of the presence of anoxic water – which is common in small and large lakes – on adsorption; and (3) the absence of a reliable water depth where ^{234}Th may be assumed to be in secular equilibrium with ^{238}U for standardization.

The dissolved ^{234}Th fraction can be scavenged by precipitation of either $\text{Fe}(\text{OH})_3$ or MnO_2 . Experiments in our laboratories have shown that using 1 mg L^{-1} of Fe^{3+} results in the scavenging of $17.6 \pm 2.6\%$ ($n = 12$) of the ^{238}U in solution in Lake Michigan. This translates to an uncertainty of $\sim \pm 0.18 \text{ dpm m}^{-3} \text{ d}^{-1}$ in supported ^{234}Th ingrowth between the time of filtration of the ferric hydroxide precipitate (t_{1b}) and the time of separation of thorium by ion-exchange chromatography (t_2), which in most instances is insignificant. In lakes or rivers with higher or lower alkalinity, a lesser or greater fraction of uranium would be carried, respectively. If the amount of uranium carried was problematic, it is possible to reduce the uranium fraction scavenged by adding ammonium bicarbonate to the water prior to acidification. While MnO_2 precipitation has the advantage over $\text{Fe}(\text{OH})_3$ in that it scavenges very little uranium, thereby eliminating the requirement for a correction for supported thorium, it is a relatively

new technique (Rutgers van der Loeff and Moore, 1999) and its effectiveness in natural freshwater systems has not yet been tested.

Both precipitates (i.e. MnO_2 and $\text{Fe}(\text{OH})_3$) scavenge high and reproducible yields of thorium (> 95%) and theoretically do not require the addition of a yield monitor. But, because we separate thorium from all other nuclides on an ion-exchange resin column and electroplate the purified thorium onto a stainless steel planchet, a yield monitor is required. Measuring low concentrations of ^{234}Th in samples from low salinity and freshwater systems requires thorium isotope isolation because of the relatively high concentrations of other naturally occurring particle-reactive beta emitting nuclides (e.g. ^{210}Pb , ^{228}Ra). Furthermore, the entire sample must be reduced to a thin, nearly weightless source because it is necessary to measure the activity of alpha emitting thorium isotopes as well.

^{230}Th and ^{229}Th are commonly used as yield monitors in the recovery of ^{234}Th . While ^{230}Th is often favored because it is a pure alpha emitter whereas ^{229}Th decays to both beta emitting progeny that inflate the gross beta count and alpha emitting progeny that can contaminate alpha detectors (Rutgers van der Loeff and Moore, 1999), the use of ^{229}Th here is preferable for several reasons. First, the activity of ^{230}Th can be quite high in freshwater environments. In Lake Michigan surface sediments, for example, the activity of ^{230}Th is approximately 0.7 dpm g^{-1} . This requires adding a substantial activity of ^{230}Th to dilute any small variation in the ambient signal. Even though ^{230}Th is a pure alpha emitter, it decays to the ground state of ^{226}Ra only 76.3% of the time (ICRP, 1983). Approximately 23% of all ^{230}Th disintegrations emit an internal conversion electron. At ~ 50 to 70 keV, these electrons have sufficient energy to pass through the (< 2 mm) air path between the sample and detector window in our beta counting system as well as the 0.08 mg cm^{-2} detector window itself (personal communication, Gamma Products, Inc.). Once in the detector, they are counted as beta events (Friedlander et al., 1964). Therefore, unless suitable shielding is added to block these conversion electrons, adding substantial activities of ^{230}Th will necessitate a significant correction to the gross beta count. In addition, we are interested in measuring the ambient activities of all thorium isotopes. Using ^{230}Th as a yield monitor would therefore require us to collect and process an additional sample as well as take extra precautions

to avoid cross-contamination in the laboratory. Finally, the problem of ^{229}Th progeny contaminating alpha detectors is not particularly severe. ^{225}Ac , the longest-lived, alpha emitting daughter of ^{229}Th , has a half life of only 10 days. Moreover, none of the alpha emitting daughters of ^{229}Th have energies that interfere with the alpha spectra of any of the thorium or uranium nuclides.

3.2. Corrections to the gross beta count

After a sample planchet is counted, corrections have to be made to the total beta count in order to accurately calculate the original sample activity of ^{234}Th . These corrections are shown in figure 1 and are discussed below.

3.2.1. Instrument background correction – The first step was simply to subtract the gas-flow proportional counter background from the gross beta count.

3.2.2. ^{229}Th beta count correction – Next, corrections were made for the contribution of beta counts from ^{229}Th , ^{228}Th , ^{230}Th , and ^{232}Th decay. It was possible to define empirical equations that described this in-growth of beta counts from separate counts of their respective isotopic sources (as outlined in section 2.3.1. above).

Beta counts from ^{229}Th decay (β_{229} , cpm) grew in at an initial rate of:

$$\beta_{229} \text{ (cpm)} = A^{229}\text{Th (dpm)} [0.0297(t_3 - t_2) + 0.2741], \quad (1)$$

for $t_3 - t_2 \leq 14.6$ days (figure 2a), where $t_3 - t_2$ was equal to the time elapsed in days between column separation (t_2) and the beta count (t_3) and $A^{229}\text{Th}$ was equal to the activity of ^{229}Th (dpm) on the sample planchet as measured by α -spectrometry.

3.2.3. ^{228}Th beta count correction – Beta counts from ^{228}Th decay (β_{228} , cpm) grew in at an initial rate of:

$$\beta_{228} \text{ (cpm)} = A^{228}\text{Th (dpm)} [0.9688 (1 - \text{EXP} (-0.1635(t_3 - t_2))) + 0.026], \quad (2)$$

where $t_3 - t_2 \leq 14.6$ days in units of days (figure 2b) and $A^{228}\text{Th}$ was equal to the activity of ^{228}Th (dpm) on the sample planchet at the time of the beta count (t_3). Because ^{228}Th decays at a rate of $\sim 3\%$ per month, corrections were also required for any decay of ^{228}Th that occurred between the beta (t_3) and alpha (t_4) counts (generally less than 2% for our samples). The experimentally observed β cpm / Th dpm relationships described by equations 1 and 2 generally agreed with the predicted in-growth of beta activity based on Bateman equations (Friedlander et al., 1964). However, the in-growth equations provided here are purely empirical and will depend on, among other factors, sample configuration, planchet material and detector window thickness.

3.2.4. *^{230}Th beta count correction* – Though not a beta emitter per se, ^{230}Th did produce a beta signal (β_{230} , cpm):

$$\beta_{230} \text{ (cpm)} = A^{230}\text{Th (dpm)} \times [0.08], \quad (3)$$

where $A^{230}\text{Th}$ was equal to the activity of ^{230}Th (dpm) on the sample planchet as determined by α -spectrometry. The source of these beta counts is discussed in sections 3.1. above and 3.2.5. below.

3.2.5. *^{232}Th beta count correction* – Determination of the beta contribution from ^{232}Th was more difficult because ^{232}Th cannot be easily separated from ^{228}Th . Therefore, the beta contribution from ^{232}Th was measured by first counting total beta emissions from a mixture of ^{232}Th and ^{228}Th , followed by counting the activity of each isotope on the sample planchet by α -spectrometry. Beta counts attributable to ^{228}Th were then subtracted from the background corrected beta count of the ^{232}Th and ^{228}Th mixture using equation 2. The remaining beta counts, attributable to ^{232}Th (β_{232} , cpm), were equal to:

$$\beta_{232} \text{ (cpm)} = A^{232}\text{Th (dpm)} \times [0.05], \quad (4)$$

where $A^{232}\text{Th}$ was equal to the activity of ^{232}Th (dpm) on the sample planchet as determined by α -spectrometry.

The apparent beta signal from each of the alpha emitting thorium isotopes (i.e. ^{229}Th and ^{228}Th (at $t_3 - t_2 = 0$), ^{230}Th , and ^{232}Th) was higher than the expected number of betas from alpha-beta cross-talk ($\sim 1.3\%$ with a ^{210}Po source). We attribute these higher beta counts to internal conversion electrons. A comparison between the number of beta counts measured per alpha decay and the number of internal conversion electron events ($E > 50 \text{ keV}$) per alpha decay (ICRP, 1983) for all four thorium isotopes showed a linear relationship ($r^2 = 0.97$) and a conversion electron counting efficiency of 30%.

3.2.6. Chemical yield and detector efficiency correction – Next, corrections were made for the overall chemical yield (extraction, separation and electrodeposition), and the efficiency of the gas-flow proportional counters. ^{234}Th activity on the planchet at the time of the beta count (^{234}Th at t_3 , dpm) was equal to:

$$A^{234}\text{Th at } t_3 \text{ (dpm)} = \beta^{234}\text{Th (cpm)} [1/(E \times ^{229}\text{Th yield})], \quad (5)$$

where $\beta^{234}\text{Th (cpm)}$ was equal to the remaining beta count after corrections for all positive bias in the total beta count, E was equal to the effective efficiency (cpm/dpm) of each of the gas-flow proportional counters ($E = 1.15$), and ^{229}Th yield was equal to the ratio of ^{229}Th recovered on the sample planchet (as determined by α -spectrometry and the known efficiency of the α -detector itself) to that added to the initial sample matrix.

3.2.7. Decay ($t_3 - t_2$) correction – The next step was to correct for the decay of ^{234}Th on the planchet between the time of the beta count (t_3) and the time of column separation (t_2)

3.2.8. Sample size correction – The activity of ^{234}Th on the sample planchet was then normalized to the initial sample size to give ^{234}Th activity in dpm L^{-1} of water or dpm g^{-1} of particles at the time of column separation.

3.2.9. ²³⁸U support correction – Next, a correction was made for ²³⁴Th activity supported by uranium. For dissolved ²³⁴Th samples, a small correction had to be made for uranium carried with the ferric hydroxide precipitate (see section 3.1. above). While it was found that corrections for ²³⁴Th supported by the decay of particle-bound ²³⁸U were generally insignificant, supported ²³⁴Th had to be taken into account for sediment samples with very low ²³⁴Th activity. These corrections are made directly from an independent measurement of uranium in the sample as described by Edgington et al. (1996).

3.2.10. Decay ($t_2 - t_1$) correction – A final correction was made for the decay of unsupported (i.e. excess) ²³⁴Th from the time of column separation (t_2) back to the time of sample collection and particle separation (t_{1a}). In instances where the dissolved ²³⁴Th fraction could not be precipitated immediately, a straightforward correction was applied for the in-growth of supported ²³⁴Th (based on the dissolved ²³⁸U activity of the sample) during the time elapsed between the initial particle separation at t_{1a} and the ferric hydroxide separation at t_{1b} .

3.3. ²³⁴Th blank analysis

Combusted blank nitrocellulose filters (0.45 μ m, 293 mm, Millipore) yielded a negligible residue, both in terms of weight and isotopic contamination.

A blank analysis of the entire dissolved fraction procedure (i.e. sections 2.1. – 2.3.) was run on 46.5 liters of deionized water that included the ferric hydroxide precipitation reaction with 55 mg Fe³⁺, 500 ml HCl (12M), and 500 ml NH₄OH (14M) and 0.24 dpm of ²²⁹Th as a yield monitor. Total sample beta activity, corrected for instrument background and ²²⁹Th derived beta activity (see section 3.2.2. above), was equal to 0.086 ± 0.064 dpm.

3.4. Verification of method and uncertainties

To test the accuracy of our approach to measuring ^{234}Th , we measured samples with ^{234}Th activities in secular equilibrium with ^{238}U . Because there is little chance of collecting a naturally occurring freshwater sample where ^{234}Th activities may be assumed to be in secular equilibrium with ^{238}U , we analyzed four ~ 1 g samples of sediment from a single sample of homogenized (14-16 cm deep) Lake Michigan sediment collected in 1991. In these samples ^{234}Th bound to the sediment must be in secular equilibrium with its parent, ^{238}U . By measuring both nuclides, any biases introduced by this approach should show as a net difference in the measured activities of the parent and daughter.

After adding 0.8 dpm ^{229}Th (NIST SRM-4328b) to each of the sediment samples, the samples were analyzed according to the methods described above and counted for gross beta activity (for four consecutive 500 minute counts) approximately 4.5 days after column separation (t_2). The results obtained in this comparison are shown in table 1.

The top section of the table details the results obtained for all of the α -active isotopes measured in each sample, including the isotopic diluent (^{229}Th) and ^{238}U . The reported activities of the thorium isotopes in dpm reflect activities of each isotope on the sample planchet based on the known efficiencies of the alpha detectors. The total recovery of thorium based on the isotopic diluent varied between 71 and 98%. Variability in the uranium activity of the sediment samples was primarily due to variability in the HCl leaching process – which is difficult to control and not a problem as far as the recovery of surface-bound unsupported (excess) ^{234}Th is concerned.

The second (middle) section of the table details the corrections for the background counts from the beta counters (first column) and the contributions from all isotopes other than ^{234}Th that will be subtracted from the initial total beta counts (first column in the bottom section of the table). The correction for detector background accounted for an average of 26% of the original beta counts, and subsequent corrections for beta counts generated by ^{229}Th , ^{228}Th , ^{232}Th and ^{230}Th further reduced the initial total beta count by an average of 9%, 31%, 4%, and 3%, respectively. These corrections are subtracted cumulatively going from left to right in the bottom section of the table. Corrections for sample yield based on total ^{229}Th recovery, gas-flow proportional counter efficiency, ^{234}Th decay between beta

counting and column separation and normalizing for sample size resulted eventually in a mean ^{234}Th activity of $0.95 \pm 0.26 \text{ dpm g}^{-1}$ (1s, n = 4) (penultimate column). Direct measurement of ^{238}U removed during the initial leaching of the sediment sample yielded an average activity of $0.92 \pm 0.09 \text{ dpm g}^{-1}$ (1s, n = 4). Subtracting the calculated ^{234}Th activities from the measured ^{238}U activities in each sample resulted in a mean excess ^{234}Th activity (final column) of $0.03 \pm 0.16 \text{ dpm g}^{-1}$ (1s, n = 4). The one sigma (1s) error based on replicate sample analyses was two times higher than the average 1s error based solely on propagated counting statistics because sampling errors and other processing uncertainties are not factored into simple propagated counting statistics (Buesseler et al., 2001). From these results, we conservatively estimate the detection limit of ^{234}Th for this method at 1.5 dpm / total sample (APHA, 1998; NCRP, 1985).

3.5. Comparison of computational methods

3.5.1. Immediate sample count method – The immediate sample count method relies on measuring the activity of ^{234}Th before significant in-growth of extraneous beta activity occurs. And while the rate of extraneous in-growth of beta activity depends ultimately on the activities of ^{229}Th , ^{228}Th , ^{230}Th and ^{232}Th deposited on the sample planchet, it also depends largely on the original isotopic composition of the sample. To determine the error associated with ignoring this fraction of the total beta count, we compare the results of ^{234}Th measurements obtained using our approach to those of the immediate sample count method for samples from Lake Michigan. These samples were collected over a period of 5 months in 2000, in water depths ranging between 5 and 40 meters, and include (1) the dissolved (<0.45 μm) fraction in the water (n = 195); (2) the suspended particle fraction in the water (n = 160); and (3) lakebed surface (0-0.5 cm) sediment (n = 65) (figure 3, *in situ* thorium activities). For ready comparison, all thorium isotope activities were normalized to 1 cpm of ^{234}Th at the time of column separation (t_2). Estimates of beta generation from the normalized α -activities of ^{229}Th , ^{228}Th , ^{232}Th and ^{230}Th were then calculated for a period of 14 days after column separation using equations 1 through 5

(figure 3, thorium beta counts over time). At one day after column separation, extraneous and apparent (non- $^{234}\text{Th} + ^{234m}\text{Pa}$) beta counts accounted for an average of $\sim 4\%$ of the total beta count from the dissolved and particle-bound water fractions (figure 3, top and middle). This percentage rose to an average of 27% in surface sediment samples, (figure 3, bottom). Moreover, the error was compounded when correcting for ^{234}Th decay between column separation (t_2) and the beta count itself (t_3). Ignoring the non- $^{234}\text{Th} + ^{234m}\text{Pa}$ beta signal in water column samples led to an average ^{234}Th overestimate of $\sim 5\%$ if the counts were completed one day after column separation. This increased to a 38% error for surface sediment samples.

3.5.2. Multiple beta count method – To compare our approach to measuring ^{234}Th with the multiple beta count method, we counted the beta activity of three suspended particle samples from Lake Michigan four times over a 114-day period after column separation of thorium (figure 4). For this method, estimates of the beta count rate (cpm) at column separation (t_2) due specifically to ^{234}Th were calculated using the slope of a regression of the last two counts (solid circles). Estimates of the ^{234}Th beta count rate at column separation using our approach were calculated from the first count of each sample (crosshatched circles). In spite of the fact that our initial counts were made 15, 17 and 3 days after column separation (figure 4; panels a, b and c respectively), agreement between the two counting methods was excellent. The mean difference in calculated initial activity (at t_2) for all three samples was 0.03 cpm with a standard error of the residual mean equal to ± 0.24 cpm. These results are important because they demonstrate that we are able to effectively account for the in-growth of non- $^{234}\text{Th} + ^{234m}\text{Pa}$ beta activity over a period of at least two weeks after column separation of thorium. Moreover, because the initial beta count can be made immediately after thorium is purified, our method reduces by up to one half the minimum initial sample activity required by the method relying on multiple beta counts.

3.6. ^{234}Th activities in water samples collected from Lake Michigan.

This technique has been used to measure ^{234}Th in over 300 water samples from Lake Michigan. These samples were collected at different seasons between 1998 and 2000 from surface waters (~ 2 to 20 m) at stations in shallow nearshore (5 m) to deepwater (150 m) environments. The results of these analyses are presented in figure 5a and b, which display the distribution of activities measured on the dissolved and particle-bound fractions. From these data it is readily seen that, the amount of ^{234}Th in either the dissolved or particle-bound fraction is a very small fraction of the expected activity in secular equilibrium with ^{238}U . The preponderance of ^{234}Th activity in the 0 - 10 dpm m^{-3} range in the dissolved fraction reflects the strong affinity of thorium for particles as well as the generally high suspended particle load in these relatively shallow systems. A similar preponderance in the frequency of low ^{234}Th activities on particles reflects the rapid flux of particles from these surface water environments.

3.7. Method application to low salinity and freshwater systems

The sample size of water or sediment needed to obtain a measurement of ^{234}Th depends ultimately on the source strength or activity of the parent, ^{238}U . In marine systems, the activity of dissolved ^{238}U correlates strongly with salinity (Chen et al., 1986) and knowledge of the latter is often sufficient for estimating potential ^{234}Th activity. In freshwater systems, however, Wahlgren and Orlandini (1982) and work we have done here show only a weak correlation between dissolved ^{238}U and conductivity in North American lakes, rivers and bogs (figure 6). Regional variations in the uranium content of weatherable minerals as well as large variations in carbonate alkalinity and dissolved organic carbon (which affect the distribution coefficient of uranium between dissolved and particle-bound states) preclude an exact correlation. Nevertheless, the correlation is strong enough to show that disequilibria between ^{234}Th and ^{238}U can be measured in all but the most pure freshwater systems.

4. Conclusions

Measuring $^{234}\text{Th}/^{238}\text{U}$ disequilibria in aquatic systems can provide answers to a host of rate-related questions regarding the behavior of particles and particle-reactive matter. Increasing the accuracy and lowering the detection limit of these measurements decreases both the uncertainty of our results and the geographical and temporal limits on where and when this isotope chronometer can be used. In this study, we presented a new approach to measuring ^{234}Th in low salinity and freshwater systems that improves upon currently used beta-counting methodologies in significant ways. By correcting for apparent beta counts (i.e. conversion electrons) our method eliminates the bias inherent in the method relying on immediate sample counting. By correcting for extraneous betas produced by the progeny of other thorium isotopes in a sample (e.g. the ingrowth of ^{212}Bi from ^{228}Th) our method eliminates the bias inherent in the method relying on weak beta absorbers, which, for ^{212}Bi at least, cannot be differentiated from or selectively absorbed in the presence of ^{234m}Pa . Finally, because we count the sample for betas only once – and can do so before the complete ingrowth of ^{228}Th progeny – our method reduces by up to one half the minimum initial sample activity required by the method relying on multiple beta counts.

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Figure Captions

FIGURE 1. A procedure for measuring low concentrations of ^{234}Th in water and sediment. Section numbers for each step of the procedure in the text are shown in brackets.

FIGURE 2. Beta ingrowth from a) ^{229}Th and b) ^{228}Th over a period of 14.6 days after thorium separation on an anion exchange resin column. The circles show the measured beta count rate (cpm, $\pm 1\sigma$ counting errors) as a function of thorium activity (dpm) measured later by α -spectrometry. Equations for the solid lines are given in the text as a) equation 1 and b) equation 2.

FIGURE 3. The contribution of beta counts from all thorium isotopes in Lake Michigan samples from top) the dissolved water fraction, middle) the particle-bound water fraction, and bottom) lakebed surface (0 - 0.5 cm) sediment. Activities (mean $\pm 1\sigma$) of the naturally occurring thorium isotopes in each of the

three sample types are shown on the left. Subsequent beta count rates for all thorium isotopes (including the isotopic diluent ^{229}Th) normalized to 1 cpm ^{234}Th at t_2 over a period of 14 days after thorium purification at t_2 are shown on the right.

FIGURE 4. ^{234}Th decay curves. In panels a – c), total beta count rates (circles) from three Lake Michigan water column samples are plotted against $e^{-\lambda t}$, where λ equals the ^{234}Th decay constant ($\lambda = 0.02876 \text{ day}^{-1}$) and t equals the time in days since thorium separation on an anion exchange resin column. The slope (m) and y-intercept (b), obtained from two-point regressions (solid line) on the last two counts of each sample (solid circles), give the initial activity of ^{234}Th (in counts per minute) at column separation and activity generated by background and decay products of the other thorium isotopes (i.e. ^{228}Th , ^{229}Th , ^{230}Th and ^{232}Th), respectively. The slight deviation of the first two counts (open circles) from the regression line is caused by the incomplete in-growth of beta activity from ^{228}Th (and ^{229}Th) decay chains. The first count in each of the three samples (cross hair) was used to make a single time-point or “ α corrected single β count” calculation of ^{234}Th activity at the time of column separation using the method we describe here.

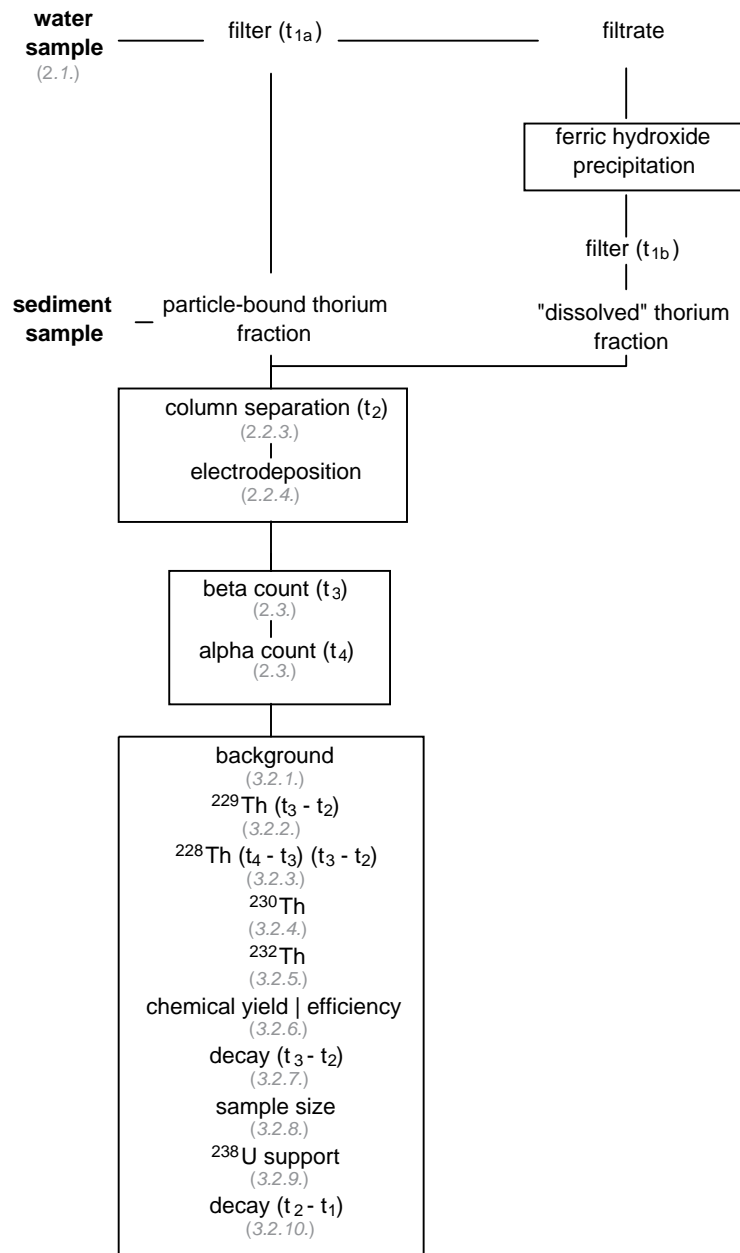
FIGURE 5. Frequency distribution of Lake Michigan ^{234}Th activities in top) the dissolved fraction ($n = 316$) and bottom) the particle-bound fraction ($n = 311$) of water samples collected between 1998 and 2000 in water column depths ranging from 5 to 150 meters.

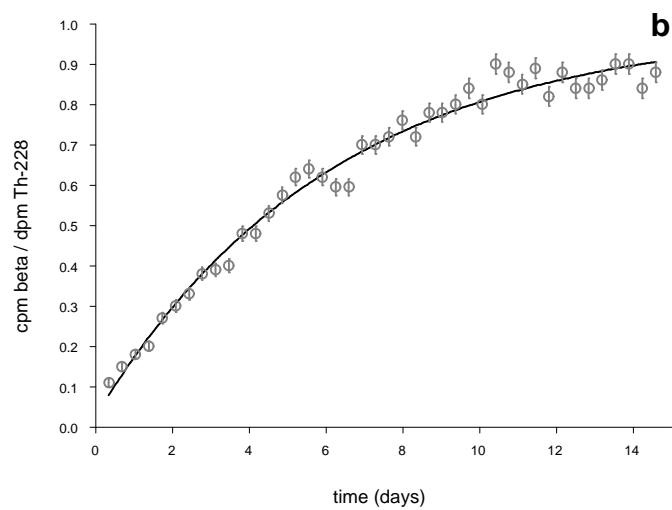
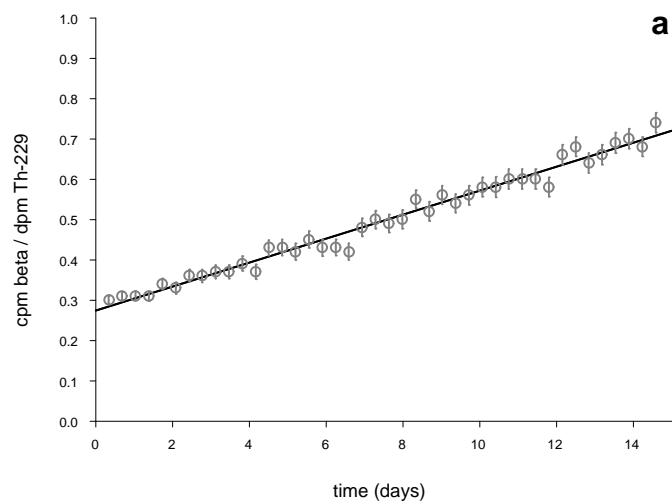
FIGURE 6. Dissolved ^{238}U activity in selected North American lakes, bogs, and rivers as a function of conductivity; ¹Wahlgren and Orlandini (1982), ²this study.

TABLE 1. Calculation of excess ^{234}Th activity on four replicate samples of homogenized Lake Michigan sediment (14-16 cm deep)

sample		²²⁹ Th dpm	²²⁸ Th dpm	²³² Th dpm	²³⁰ Th dpm	²²⁹ Th recovery %				²³⁸ U dpm/g	
alpha counts	1	0.60 ± 0.01	1.53 ± 0.02	1.42 ± 0.02	1.15 ± 0.02	73 ± 2				0.80 ± 0.04	
	2	0.59 ± 0.01	1.66 ± 0.02	1.55 ± 0.02	1.34 ± 0.02	71 ± 2				1.03 ± 0.05	
	3	0.80 ± 0.02	1.87 ± 0.02	1.90 ± 0.02	1.56 ± 0.02	98 ± 2				0.94 ± 0.05	
	4	0.74 ± 0.02	1.86 ± 0.02	1.84 ± 0.02	1.50 ± 0.02	90 ± 2				0.91 ± 0.05	
sample		beta background	β ₂₂₉ ¹ cpm	β ₂₂₈ ² cpm	β ₂₃₂ ³ cpm	β ₂₃₀ ⁴ cpm	recovery ⁵ factor	decay factor	sample mass factor		
beta count correction	1	0.73 ± 0.02	0.24 ± 0.01	0.82 ± 0.02	0.07 ± 0.01	0.09 ± 0.01	1.20 ± 0.02	1.14	0.96		
	2	0.77 ± 0.02	0.24 ± 0.01	0.89 ± 0.02	0.08 ± 0.01	0.11 ± 0.01	1.22 ± 0.02	1.14	0.93		
	3	0.76 ± 0.02	0.33 ± 0.01	1.00 ± 0.02	0.09 ± 0.01	0.12 ± 0.01	0.89 ± 0.02	1.14	0.95		
	4	0.84 ± 0.02	0.30 ± 0.01	1.00 ± 0.02	0.09 ± 0.01	0.12 ± 0.01	0.97 ± 0.02	1.14	0.94		
sample	initial β count cpm	- bkgd cpm	-β ₂₂₉ cpm	-β ₂₂₈ cpm	-β ₂₃₂ cpm	-β ₂₃₀ cpm	²³⁴ Th at t ₃ dpm/sample	²³⁴ Th at t ₂ dpm/sample	²³⁴ Th dpm/g	excess ²³⁴ Th dpm/g	
beta count	1	2.47 ± 0.04	1.74 ± 0.04	1.49 ± 0.04	0.67 ± 0.05	0.60 ± 0.05	0.51 ± 0.05	0.61 ± 0.06	0.70 ± 0.07	0.67 ± 0.06	-0.13 ± 0.08
	2	3.07 ± 0.04	2.30 ± 0.04	2.06 ± 0.05	1.18 ± 0.05	1.10 ± 0.05	0.99 ± 0.05	1.21 ± 0.07	1.38 ± 0.08	1.29 ± 0.07	0.26 ± 0.09
	3	3.26 ± 0.04	2.49 ± 0.04	2.17 ± 0.05	1.16 ± 0.05	1.07 ± 0.05	0.94 ± 0.05	0.84 ± 0.05	0.96 ± 0.06	0.92 ± 0.05	-0.02 ± 0.07
	4	3.24 ± 0.04	2.39 ± 0.05	2.09 ± 0.05	1.09 ± 0.05	1.00 ± 0.05	0.88 ± 0.05	0.85 ± 0.05	0.97 ± 0.06	0.92 ± 0.06	0.01 ± 0.07

^aThe initial (gross) beta count (lower left corner) is progressively corrected for beta interferences outlined in section 3.2 of the text. Beta count corrections with superscripts 1-5 were calculated using the activities of the alpha-emitting thorium isotopes and equations 1-5 in the text. Errors for each value reflect propagated counting errors ($\pm 1s$) only.

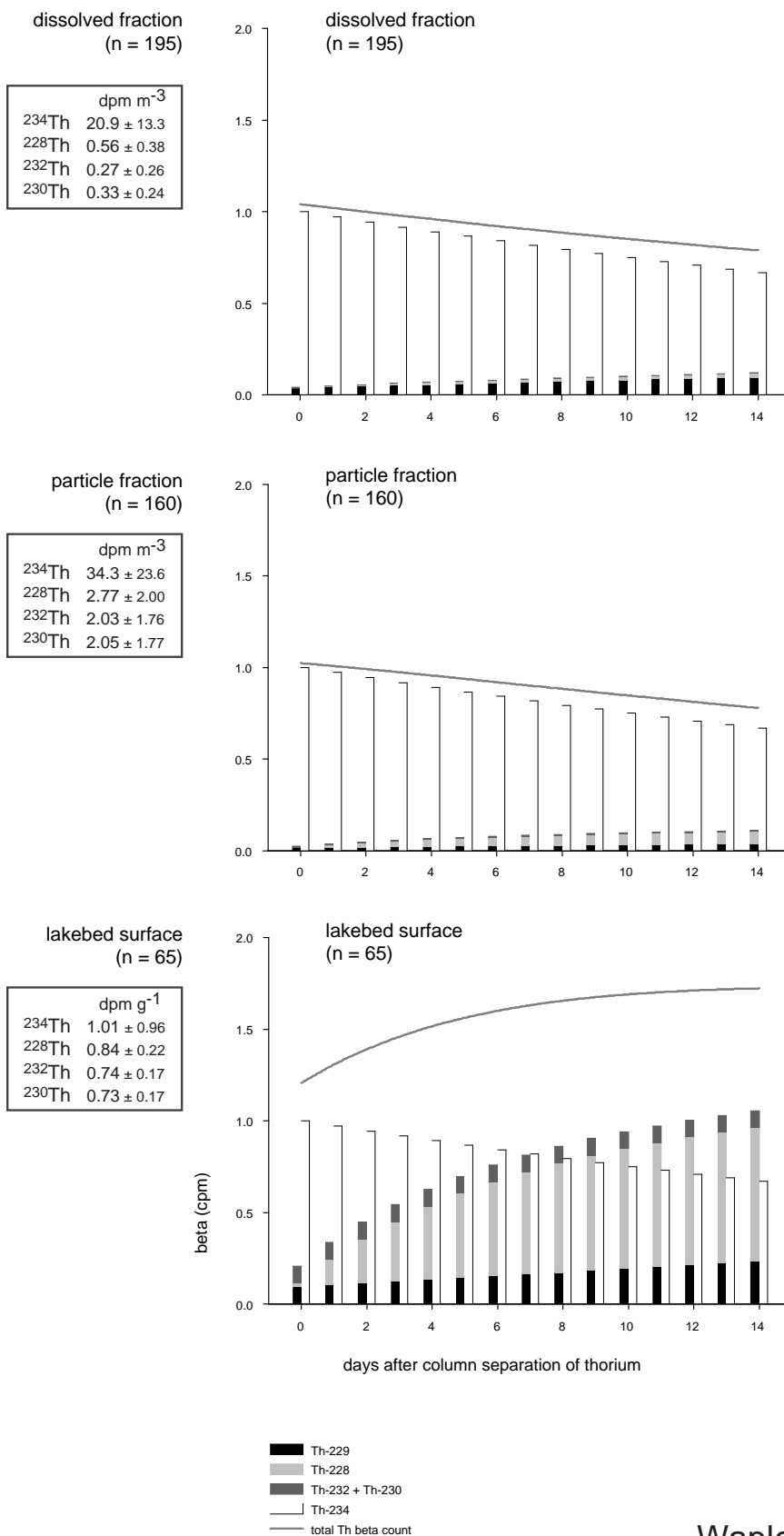




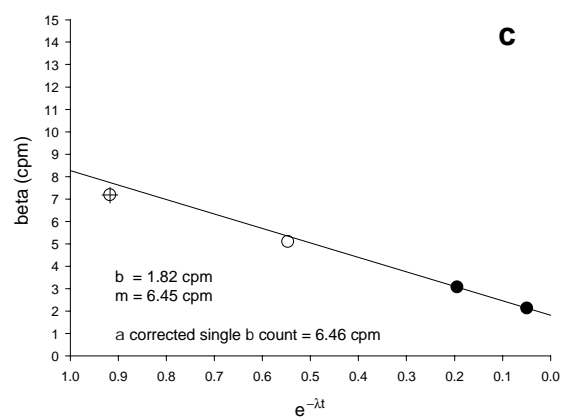
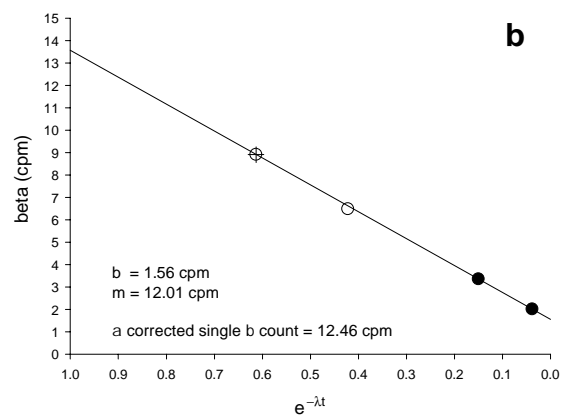
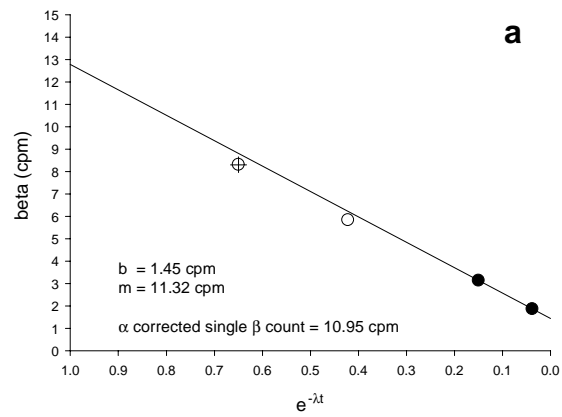
Waples Figure 2

in situ thorium activities

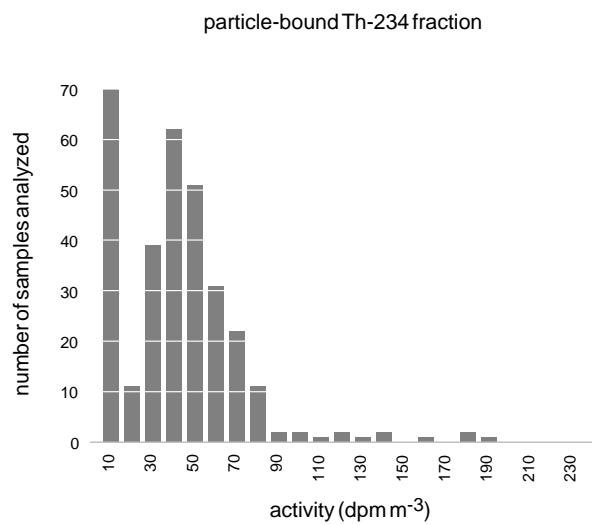
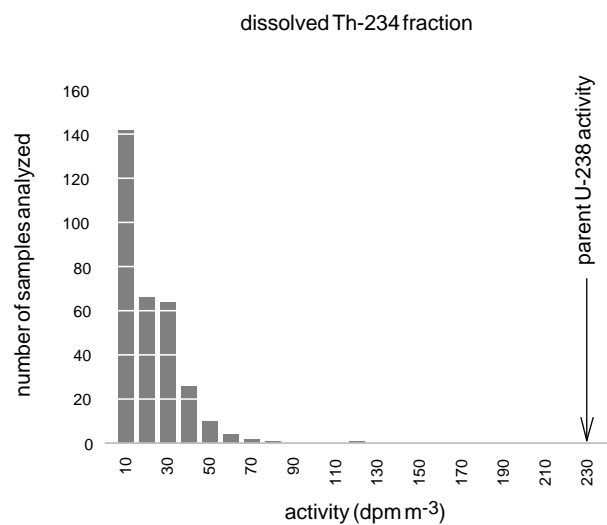
thorium beta counts over time



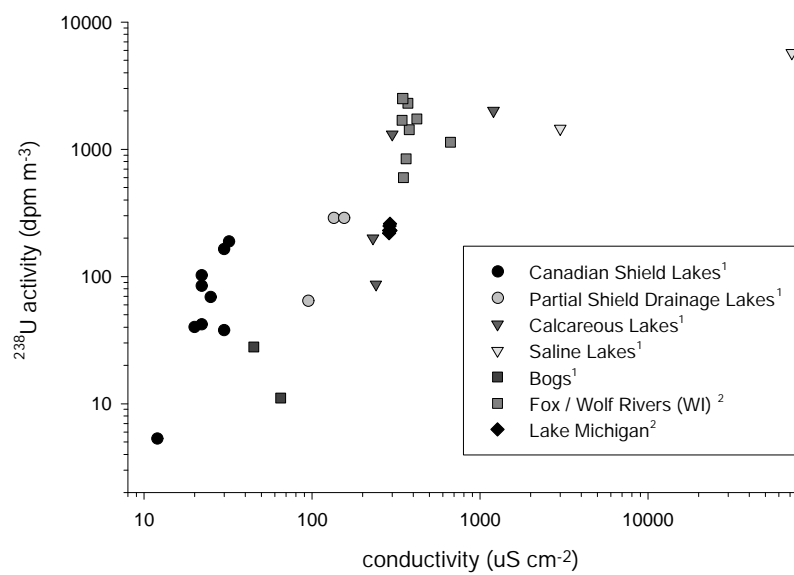
Waples Figure 3



Waples Figure 4



Waples Figure 5



Waples Figure 6